

Electrooxidation of primary alcohols on smooth and electrodeposited platinum in acidic solution

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Abstract

The electrooxidation of primary alcohols with four to eight carbon atoms on black Pt electrodeposits on gold/quartz, and on commercial bright platinum/quartz electrodes in perchloric acid solution, was studied by cyclic voltammetry (CV) and with the electrochemical quartz crystal microbalance (EQCM). Alcohol physisorption and Pt oxide reduction by chemical reaction with the alcohols were observed, both processes increasing with increasing chain length of the alcohol. Hexanol addition at 0.4 V versus SCE, the potential at which Pt oxidation starts, or higher potentials produced both an anodic current of hexanol electrooxidation and a mass decrease of bright Pt/Q electrodes, which shows unequivocally that the alcohol reduces the Pt oxide chemically.

Keywords: Primary alcohols; Electrooxidation; EQCM; Platinum electrode

1. Introduction

Most studies of the electrooxidation of oxygen-containing organic compounds have been carried out with platinum, due to its high activity and low corrosion rate [1], and usually with methanol as substrate, with the goal of achieving a commercially viable direct methanol fuel cell [2]. Methanol electrooxidation on Pt involves chemisorbed CO, a reaction product that poisons the electrode surface, and also another hydrogen-containing adsorbed intermediate (HCO/COH) [1]. With alcohols with two or more carbon atoms cleavage of a C- α C bond can occur [3].

In the electrooxidation of ethanol on porous Pt, Schmidt et al. [4] established by DEMS that, with ethanol in solution, in the positive scan both CO₂ and ethanol are produced, and methane and ethane in the negative scan. The same group found [5], also by DEMS, that in ethanol-free solution the electrooxida-

tion of the chemisorption products of ethanol on porous Pt yields CO₂ as the sole oxidation product, and again methane and ethane as reduction products. Schell [6] and Krausa and Vielstich [7] have postulated that chemisorbed CO reacts with weakly bound water and/or chemisorbed OH to give CO₂ [8]. Li and Sun [9] and Li et al. [10] found by FTIRS that adsorbed CO was the main poisoning species in the electrooxidation of 1-butanol on Pt in acid media. Li et al. [10] claim, based on ex-situ XPS studies, that in the electrooxidation of small primary alcohols (C₁ to C₄) on Pt, the Pt oxides formed at potentials lower than 1.0 V (SCE), said to be PtOH, Pt(OH)₂ and PtO, probably behave as active species for alcohol oxidation, while the Pt surface oxides formed at potentials higher than 1.0 V (SCE), said to be Pt(OH)₃ and PtO₂, would act as poison species.

It is usually assumed that the activity of a Pt electrode depends on its crystalline structure, surface texture, roughness, grain size, etc. [11,12]. For most electrocatalytic processes the specific activity (i.e. the activity per unit hydrogen electrode area) of platinized platinum (Pt/Pt) electrodes is lower than that of smooth Pt [13], although it has been reported that graphite-supported Pt is very resistant to poisoning [14].

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The electrochemical quartz crystal microbalance (EQCM) can give valuable information, not only about mass changes of the electrode, but also about interfacial friction, surface roughness and thin film viscoelasticity [15]. Wilde and Zhang [16] have reported that in methanol oxidation at Pt/Au/Q electrodes the poisoning by strongly adsorbed species is accompanied by a *decrease* in mass relative to the background electrolyte, this decrease being attributed to a displacement by the poisoning species of water and anions. Daikhin et al. [17] found that the specific adsorption of pyridine on gold electrodes in water and butanol involved not only a mass change of an adsorbed layer rigidly coupled to the oscillating surface, but also a finite slippage at the adsorbed layer | water interface.

The study of higher alcohols could shed light on the structure of the metal | electrolyte interface in the presence of molecules with amphiprotic character. In this work we have studied the electrooxidation on Pt of primary alcohols with four to eight carbon atoms to determine the influence of chain length. Black Pt electrodeposits on gold/quartz and bright commercial Pt/Q electrodes were used for studying the effect of the surface texture and roughness of Pt on alcohol electro-oxidation.

2. Experimental

2.1. Reagents and equipment

Primary alcohols: 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol were of analytical grade (Aldrich) and used without further purification. All the solutions were freshly prepared with bidistilled water. The required alcohol concentrations were obtained by injection with a syringe of the required volume of alcohol in the 0.5 M HClO₄ supporting electrolyte. The experiments were carried out at room temperature under a nitrogen atmosphere.

The electrochemical equipment consisted of a Wenking POS73 Potentiostat controlled by a CAEM Instrumentation electrochemical interface interfaced to a 486 PC, or an Elchema PS 205 potentiostat, both with suitable software for fully automated control of the experiments and data acquisition. An EQCM (EQCM-501 from Elchema) with 10 MHz AT-cut quartz oscillators was used. The calibration was made by anodic stripping of Cu deposited by cyclic voltammetry (CV) at 0.1 V s⁻¹ from 10 mM Cu(II) solution in 0.1 M HNO₃. The calibration constant was $dm/df = 4.4 \text{ ng cm}^{-2} \text{ Hz}^{-1}$. All potentials were measured against, and are referred to, a saturated calomel electrode (SCE).

2.2. Working electrodes

Two types of Pt electrodes were used for the EQCM measurements: (i) black Pt/Au/Q electrodes obtained by electrodeposition at 1 mA cm⁻² from 2 mM H₂PtCl₆ (Aldrich) in 0.5 M H₂SO₄ on an Elchema 10 MHz AT-cut, Au-covered quartz crystal, the mass electrodeposited being controlled by EQCM; and (ii) an Elchema 10 MHz AT-cut quartz crystal with a bright Pt deposit on both faces (Pt/Q electrode). The roughness factors (R_F) were calculated from the hydrogen desorption charge, taking a value of 0.21 mC cm⁻² for a hydrogen monolayer. Mass changes and current densities were referred to the geometric area.

The black Pt/Au/Q electrodeposited electrodes were activated by 10 potential cycles in 0.5 M H₂SO₄ at 0.1 V s⁻¹. Wilde et al. [18] and Ureta-Zañartu et al. [19] have reported that the EQCM response in the hydrogen region of electrodeposited Pt electrodes can change with prolonged cycling of the electrode, although the CV shows no appreciable changes. Therefore, the black Pt/Au/Q electrodes were used only until the mass increase due to hydrogen adsorption began to increase above its usual value.

Two procedures of alcohol addition were used. In one procedure the potential was held at -0.22 V, after which the required volume of alcohol was injected in the cell with a syringe, the electrolyte was stirred with N₂ to achieve homogenization, and the mass was allowed to stabilize. This procedure took 240 s, after which a positive potential scan was started. In the other procedure the electrode was introduced at open circuit into the alcohol solution previously deaerated by nitrogen bubbling.

3. Results

3.1. Results obtained with the black Pt electrodeposits

3.1.1. Characterization of the black Pt electrodeposits

Platinum was electrodeposited on the Au/Q electrode and the black Pt/Au/Q deposit was activated as described in Section 2. The Pt deposits had a mass of about 28 μg cm⁻², a roughness factor R_F between 13.1 and 29.3, a specific area between 11.7 and 26.2 m² g⁻¹, and a particle diameter (evaluated according to Mikhaylova et al. [20]) between 5.9 and 2.6 nm. Electrodes with a higher R_F would exceed the limit of applicability of the Sauerbrey equation [21].

3.1.2. First positive scan with black Pt electrodeposits after alcohol addition at -0.22 V

The first positive scan at 0.02 V s⁻¹ of a black Pt/Au/Q electrode in 0.5 M HClO₄ in 10 mM butanol (A, solid line) and 10 mM heptanol (B, solid line) solutions, after

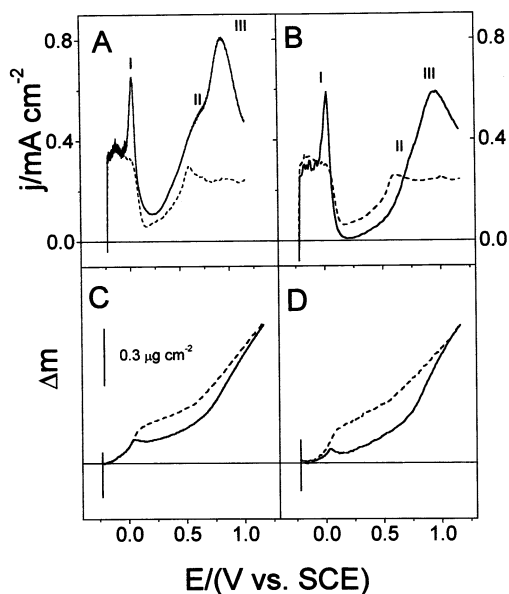
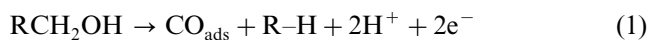


Fig. 1. First positive voltammetric scan (A and B), and simultaneously recorded mass response (C and D), of a black Pt/Au/Q electrode at 0.02 V s^{-1} in 0.5 M HClO_4 in the absence (dashed lines) and in the presence (solid lines) of $10 \text{ mM } n$ -butanol (A and C) and $10 \text{ mM } n$ -heptanol (B and D). The alcohols were added while the electrode was held at -0.22 V . $R_F = 13.1$.

addition of the alcohol at -0.22 V , and the simultaneously recorded mass change (C and D, respectively) are given in Fig. 1. The dashed lines show the background response in base electrolyte. Holding the potential at -0.22 V for 240 s led to a slight poisoning of the electrode, as is apparent from the current increase in the double layer region of the CV. However, this holding time could not be reduced because it was the minimum time required for mass stabilization before and after alcohol addition.

In the first positive scan the alcohols produced no decrease of the hydrogen desorption charge, in the same way as with smooth Pt electrodes [1]. Two peaks of alcohol oxidation appear (peaks I and III) and a shoulder (peak II) at the foot of peak III. Petry et al. [22] were the first to report peak I for $0.05 \text{ M CH}_3\text{OH}$ (admitted at 50 mV vs. RHE) in $0.05 \text{ M H}_2\text{SO}_4$ at a Pt/Pt electrode, and attributed it to methanol dehydrogenation. Krausa and Vielstich [7], Xia et al. [23] and Vielstich and Xia [24] have shown by DEMS that, in the case of methanol, peak I is due to its electrooxidative dehydrogenation on a Pt surface that is oxide-free, leading to chemisorbed CO. In the case of ethanol or higher alcohols the reaction would be:



The chemisorbed CO produced by reaction (1) can be evaluated as $\theta_{\text{CO}}^{\text{I}} = (Q_{\text{H}} - Q_{\text{H}}^{\circ})/2Q_{\text{H}}^{\circ}$, where Q_{H} and Q_{H}° represent the charge between -0.23 and 0.15 V in the presence and absence of the alcohol, respectively. This

CO coverage should coincide with the fraction of the surface H-sites covered by CO, $\theta_{\text{CO}}^{\text{H}}$, determined from the decrease of the hydrogen charge (see below), since, as is well known, most of the CO chemisorbed on Pt in acid media is in the linear (on-top) configuration. $\theta_{\text{CO}}^{\text{I}}$ is low, about 0.1, for butanol–hexanol, and still lower, 0.012, for heptanol (Table 1).

We can define an oxidation parameter, OP, as $\text{OP} = (Q_{\text{ox}} - Q_{\text{ox}}^{\circ})/Q_{\text{H}}^{\circ}$ where Q_{ox} and Q_{ox}° are the charges between 0.3 V and the positive limit of the scan in the presence and absence of the alcohol, respectively. Thus, the OP parameter represents the extra number of electrons transferred per surface H-site in the potential window between 0.3 V and the positive limit of the scan due to the presence of alcohol. The OP of heptanol is 30–45% of the OP of the lower alcohols (Table 1). This influence of the chain length will be discussed below.

The mass response in the absence of alcohol has been explained by Gloaguen et al. [25], Wilde et al. [18] and Santos et al. [26] in terms of water and anion adsorption/desorption at low potentials, and of Pt oxide formation at higher potentials. The differences in the mass change in the H-desorption and double layer potential regions among different groups can be attributed, at least in part, to differences in electrode preparation which can affect the rugosity, pore size, etc. [19], and have been discussed by Wilde et al. [18], who claim that prolonged potential cycling brings about a change of the structure of the Pt deposits.

For the four alcohols tested no mass changes were observed upon alcohol admission at -0.22 V , even for octanol, which shows unequivocally that at -0.22 V alcohols do not physisorb on the electrodeposited Pt. Therefore, in Fig. 1C and D the initial masses at -0.22 V in the absence (dotted line) and the presence (solid line) of the alcohol have been made to coincide.

The mass change in the hydrogen region is unaffected by the alcohols (Fig. 1C and D), which shows that no organic adsorbates are formed in this region. The alcohols produce a slight mass decrease at the potential of peak I, 0.04 V , due to the formation by reaction (1) of adsorbed CO, which inhibits water and/or anion adsorption at the electrode surface, as described by Wilde and Zhang [16] for methanol. At higher potentials the

Table 1

Parameters obtained from the first positive scan at 0.02 V s^{-1} of a black Pt/Au/Q electrode in 0.5 M HClO_4 , 10 mM alcohol, with alcohol admission at -0.22 V (Fig. 1)

Alcohol	$\theta_{\text{CO}}^{\text{I}}$	OP	$\Delta m/\text{ng cm}^{-2}$ at 0.15 V
Butanol	0.108	4.4	89
Pentanol	0.084	4.5	150
Hexanol	0.096	6.6	166
Heptanol	0.012	2.0	158

$R_F = 13.1$.

mass in alcohol (solid line) is lower than the mass in supporting electrolyte, the mass decrease at 0.15 V produced by the alcohol being 89 ng cm^{-2} for butanol and 158 ng cm^{-2} for heptanol (see Table 1), indicating that the more hydrophobic heptanol displaces a greater amount of water and anions from the interface.

For all the alcohols studied, the difference between the mass at the positive and negative limits of the first scan was the same in the presence and absence of the alcohols, which, since there was no alcohol adsorption at the initial potential of -0.22 V , as said above, shows that the mass at the end of the first positive scan is the same in the presence and absence of the alcohols, indicating that the amount of Pt oxide formed is unaffected by the alcohols, and, furthermore, that no organic residue is present on the surface at the positive limit.

With these black Pt electrodes, usually, but not always, peak I appears in the first potential scan even if the alcohols are added at open circuit. Therefore, the presence of this peak I must depend on the structure of the Pt electrodeposit, which is not easy to control for very thin films, obtained with only a few minutes of electrolysis. The presence or absence of peak I is perfectly correlated with the mass change in the hydrogen region: in the former case the mass in the presence and in the absence of the alcohol is the same, irrespective of the admission potential, while in the latter case the mass in alcohol is lower than that in supporting electrolyte, indicating that dissociative chemisorption of the alcohol has occurred, blocking both the electrooxidative dehydrogenation of the alcohol and the adsorption of water and anions (not shown).

3.1.3. Second CVs with black Pt electrodeposits after alcohol admission at -0.22 V

Fig. 2A and B shows the second CV cycles (from -0.22 to 1.2 V) obtained after the positive scan described in Section 3.1.2 followed by 30 s of nitrogen bubbling at open circuit in order to restore the alcohol concentration at the electrode surface, and the simultaneously recorded mass response (Fig. 2C and D). The hydrogen region is little affected by alcohol (the decrease of Q_H values is $< 10\%$), as in the first scan after alcohol admission at -0.22 V (Fig. 1A and B), but peak I does not appear now. With butanol the shoulder II is better defined and peak III increases as compared with the first positive scan. In the negative scan the Pt oxide reduction peak is smaller than in base electrolyte, and a butanol oxidation peak appears (peak IV), which would seem to indicate that the decrease of the Pt oxide reduction peak is due to the simultaneous occurrence of butanol electrooxidation. The simultaneity of the two reactions is more evident for heptanol (Fig. 2B), for which the peak of Pt oxide reduction nearly disappears. However, with heptanol, peak IV barely appears, which suggests

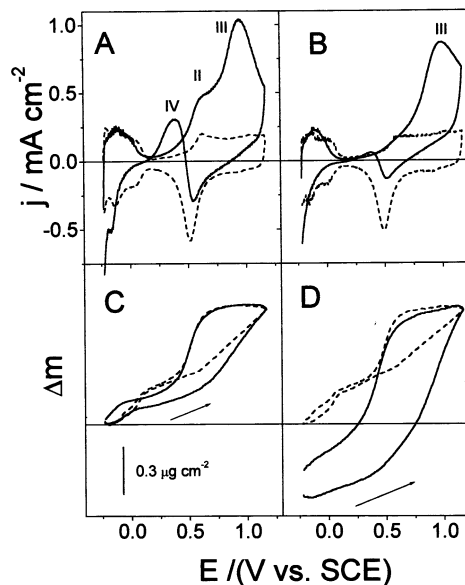


Fig. 2. Second CV after alcohol admission at -0.22 V (A and B), and simultaneously recorded mass response (C and D), of a black Pt/Au/Q electrode at 0.02 V s^{-1} in 0.5 M HClO_4 in the absence (dashed lines) and in the presence (solid lines) of 10 mM n-butanol (A and C) and 10 mM n-heptanol (B and D). $R_F = 13.1$.

that the decrease of the Pt oxide reduction peak is due to a *chemical* reaction of the Pt oxide with the alcohol, as will be shown below to be the case.

In Fig. 2C and D the mass curves in the absence and the presence of the alcohol have been made to coincide at the positive potential limit. For butanol (Fig. 2C), in the second positive scan the mass increase in the hydrogen desorption region is unaffected by the alcohol up to 0.03 V , at which potential butanol produces a small decrease of the hydrogen desorption charge (Fig. 2A) and a noticeable mass decrease, similar to that observed with an admission potential of -0.22 V (Fig. 1C), i.e. for butanol the presence or absence of peak I does not affect the mass increase up to 0.03 V .

Heptanol shows a CV (Fig. 2B) similar to that of butanol, but its mass curve (Fig. 2D) is completely different, the difference between the masses at the positive and negative limit of the scan being about 65% higher in the presence of heptanol than in its absence, while in the case of butanol this difference is the same as in base electrolyte. The coverage by all adsorbates (mainly CO [9,10]) that are stable in the hydrogen potential region can be evaluated as $\theta_{\text{CO}}^{\text{H}} = (Q_{\text{H}}^{\circ} - Q_{\text{H}}) / Q_{\text{H}}^{\circ}$, and is given for the four alcohols in Table 2. It increases with increasing chain length up to hexanol, which points to an increasing physisorption previous to the dissociative chemisorption. The decrease of $\theta_{\text{CO}}^{\text{H}}$ for heptanol as compared with hexanol is perhaps due to the fact that the concentration is near its solubility limit. $\theta_{\text{CO}}^{\text{H}}$ is 60% higher for heptanol than for butanol, which could be responsible, at least

Table 2

Parameters obtained from the second positive scan at 0.02 V s^{-1} of a black Pt/Au/Q electrode in 0.5 M HClO_4 , 10 mM alcohol (Fig. 2)

Alcohol	$\theta_{\text{CO}}^{\text{H}}$	OP
Butanol	0.17	5.20
Pentanol	0.37	5.62
Hexanol	0.49	5.45
Heptanol	0.27	2.64

$$R_F = 13.1.$$

partially, for the lower mass at the beginning of the scan with heptanol.

With butanol the mass is the same at the beginning and the end of the CV, i.e. a complete potential cycle does not alter the mass. On the contrary, with heptanol (Fig. 2D) the mass at the end of the second CV is considerably higher than that at the beginning, i.e. there has been an irreversible mass increase. Furthermore, the mass difference in the double layer region between the mass in the negative and positive scans is much larger than with butanol, pointing to a profound modification of the structure of the double layer.

At the beginning of the negative sweep the mass is barely affected by the presence of heptanol down to 0.5 V (Fig. 2D), at which potential reduction of Pt oxide starts, but the mass decrease between 0.5 and 0.15 V is much higher in the presence of heptanol, probably because the adsorption of the rather hydrophobic heptanol (which at 10 mM is near its solubility limit) decreases the adsorption of water and/or anions greatly.

An interesting parameter from the EQCM results is the $\partial(\Delta m)/\partial Q$ slope obtained from a Δm versus Q plot, as shown in Fig. 3. For faradaic processes in which the reaction product is desorbed or deposited on the electrode this slope should be M/nF (mass change (in grams) per mole of electrons transferred), where M is the molar mass of the electroadsorbed species, n the number of electrons transferred, and F is Faraday's constant (see Table 3). In Fig. 3A–C the Δm versus Q plots for the first (solid line) and the second (dashed line) positive scans for a Pt/Au/Q electrode in the absence (Fig. 3A) and the presence of 10 mM butanol (Fig. 3B) and 10 mM heptanol (Fig. 3C) are given. Arrows labelled 1, 2 and 3 indicate the positive limits of weak (-0.1 V) and strong (0.1 V) hydrogen adsorption, and of the double layer region (0.5 V), respectively. In Fig. 3B and C only the initial region of the curves is plotted in order to obtain a better resolution in the hydrogen region.

In base electrolyte the mass curve in the second scan is shifted towards smaller charges and smaller masses as compared with the mass curve for the first scan (dashed and solid curves, respectively, in Fig. 3A). The mass difference, which appears in the hydrogen region and remains practically constant at higher potentials, prob-

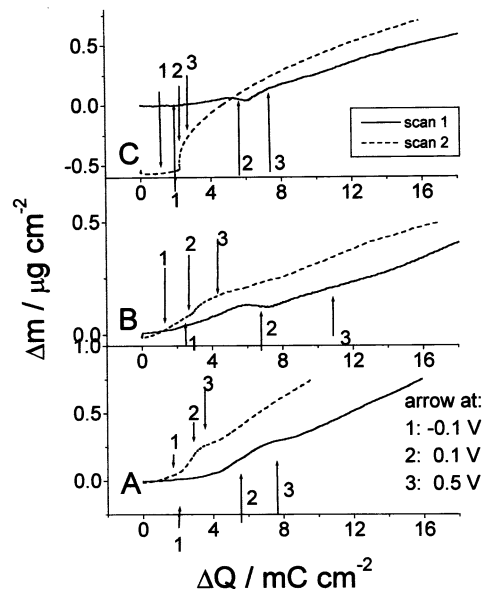


Fig. 3. Plot of mass (Δm) vs. charge (Q) values from EQCM data obtained in the first positive scan after alcohol addition at -0.22 V (solid line) and in the second positive scan (dashed line). (A) Base electrolyte; (B) 10 mM butanol; (C) 10 mM heptanol. The arrows define the following potential regions: weakly adsorbed hydrogen, region to the left of arrow 1; strongly adsorbed hydrogen, region between arrows 1 and 2; double layer, region between arrows 2 and 3; and Pt oxidation, region to the right of arrow 3.

ably stems from the adsorption of impurities, as inferred from the high double layer current in the first scan (Fig. 1A and B). Two slopes in the hydrogen desorption region, corresponding to the weakly (H_W) and strongly (H_S) adsorbed hydrogen, are clearly defined. In the first scan a positive slope of nearly 8 g per mole of electrons transferred (see Table 3) was obtained for strongly adsorbed hydrogen, in agreement with Visscher et al. [27]. Since the desorption of hydrogen should produce a negative slope of 1 g per mole of electrons transferred, it is clear that the mass increase must correspond to the adsorption of anions and water on the H-free Pt sites. The adsorption of anions and water continues in the double layer (d.l.) region, and the slope in the Pt oxide formation region (column 'ox' in Table 3) is 5.8 g mole of electrons transferred, somewhat lower than those given by Xia and Birss [28,29], probably due to the effect of adsorbed impurities, since the slope in the second scan, 8.4 g mole of electrons transferred, is in agreement with these references, and with the value of 8 g mole of electrons transferred expected for the formation of PtO or PtO₂. In the second scan the values obtained for weakly and strongly adsorbed hydrogen are 3.18 and 18.04 , respectively. These values are much higher than the corresponding ones in the first scan, which is due to a charge decrease much larger than the mass decrease, both as compared with the first scan.

In the first positive scan in the presence of the alcohols (Fig. 3B and C) the $\Delta m/\Delta Q$ curves are very

Table 3

Mass change per mole of electrons transferred obtained as the slopes of the Δm vs. ΔQ plots in Fig. 3

Alcohol	First scan				Second scan				
	H _W	H _S	CO	d.l.	ox	H _W	H _S	d.l.	ox
Base	0.97	7.9	–	Variable	5.80	3.18	18.04	–	8.40
Butanol	2.41		–0.67	2.22	2.40		3.96	3.00	1.97
Pentanol	1.35		–3.86	3.00	2.32		–	5.02	1.93
Hexanol	0.10		–1.74	3.09	1.93		–	7.24	2.90
Heptanol	1.93		–2.32	3.86	3.18		–		5.11

The alcohol concentration was 10 mM.

similar to that in base electrolyte. There is a small mass decrease near arrow 2, which is the region of peak I in the CV (see Fig. 1), and therefore this mass decrease should be due to the formation of adsorbed CO with displacement of adsorbed ions and/or water molecules. For this reason only the slope of the weakly adsorbed hydrogen could be evaluated (Table 3).

In the second scan in the presence of the alcohols the mass decrease in the hydrogen region, as compared with the mass in the first scan, appears first with pentanol, and increases with increasing chain length. Only for butanol could the hydrogen slope be evaluated in the second scan (see Fig. 3B and Table 3). While for butanol the mass increases monotonically over the whole potential scan, for pentanol–heptanol there is an initial region of constant mass that extends over the whole hydrogen region in base, and is followed by a short, nearly vertical segment. This mass increase without significant charge transfer clearly indicates that, once hydrogen desorption has been completed, pentanol–heptanol physisorption takes place on this H-free Pt surface. Furthermore, the second CVs in heptanol and base electrolyte shown in Fig. 2D practically coincide over the whole double layer region, which indicates that the physisorbed heptanol is not electrooxidized in this potential range. On the contrary, butanol is electrooxidized in the double layer region, as can be seen in the CV in Fig. 2A, and, consequently, from the horizontal distance between arrows 2 and 3 (double layer region) in Fig. 3B.

The slopes in columns d.l. and ox in Table 3 were obtained from the double layer region (between arrows 2 and 3) and oxide region (to the right of arrow 3), respectively, in Fig. 3. The slopes in the ox region in both the first and second scans are lower in the presence of alcohols than that of Pt oxide formation in base electrolyte, as was to be expected, since a high fraction of the charge transferred, namely $OP/(1+OP)$, goes towards alcohol electrooxidation, a process which does not contribute to a mass increase. This slope is markedly higher for heptanol than for the other alcohols, both in the first and second scans, in agreement with the fact that the OP is markedly lower for heptanol, also both in the first and second scans.

With the higher alcohols, and especially for heptanol, the mass at the beginning of the second scan was lower than that in the first scan, indicating that with increasing chain length there is an increasing physisorption of the alcohol. We return to this point below.

3.1.4. Effect of the scan rate on the second CV with black Pt electrodeposits with alcohol admission at open circuit

In these experiments the alcohol was added at open circuit, a ‘stabilizing’ CV was carried out from the negative potential limit, the electrolyte was stirred by nitrogen bubbling for 1 min to reestablish solution homogeneity, and a second CV was carried out and recorded simultaneously with the mass curve. With this procedure peak I, which with electrodeposited Pt generally appears in the first scan even with alcohol admission at open circuit, as noted above, does not appear in the second CV, and so its interference with the other peaks in the CV is avoided.

Fig. 4 shows the second CVs and the mass curves for black Pt/Au/Q electrodes in 0.5 M HClO₄ (Fig. 4A and D), in 0.5 M HClO₄ with 20 mM butanol (Fig. 4B and E) and 20 mM *n*-pentanol (Fig. 4C and F).

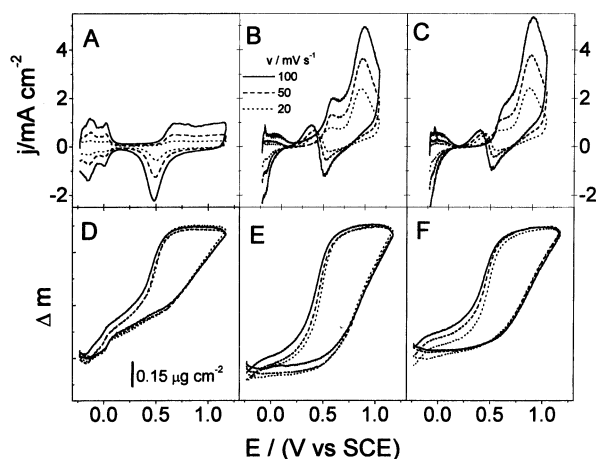


Fig. 4. Second CV (A, B and C) and simultaneously recorded mass response (D, E and F) of a black Pt/Au/Q electrode at different scan rates in 0.5 M HClO₄ (A and D) and in 0.5 M HClO₄ with 20 mM *n*-butanol (B and E) and 20 mM *n*-pentanol (C and F). The alcohols were added to the electrolyte while the electrode was at open circuit and the scans were begun at the negative limit. $R_F = 29.3$.

E) and in 0.5 M HClO₄ with 20 mM pentanol (Fig. 4C and F). In base electrolyte, with increasing scan rate the potential at which Pt oxidation starts, as reflected by the corresponding mass increase, is practically independent of the scan rate, but the mass decrease corresponding to the reduction of the Pt oxide is shifted to more negative potentials, i.e. it becomes more irreversible (Fig. 4D). This scan rate independence of the Pt oxide formation, and dependence of the Pt oxide reduction (both types of behaviour obviously to be expected from the corresponding CVs), is unaffected by butanol (Fig. 4E) or pentanol (Fig. 4F). As for the hydrogen and double layer regions, in which in 0.5 M HClO₄ the mass increases with the potential, they show almost no mass changes in the presence of the alcohols, especially at the higher scan rates, from which it can be inferred that there is an alcohol physisorption that inhibits the adsorption of water and/or anions. In the presence of butanol or pentanol the mass change after a complete CV (second scan) is almost zero, independently of the scan rate.

The mass change per mole of electrons transferred, obtained from the slopes of the linear segments of Δm versus ΔQ plots, are given in Table 4. Both in the absence and presence of alcohols the mass decreased with increasing potential in the region of weakly adsorbed H, and it was not possible to evaluate a slope. In base electrolyte, the slope in the region of strongly adsorbed H decreased monotonically with decreasing scan rate. The slopes in the Pt oxide region are in the range 7.6–6.7 g per mole of electrons transferred, in fair agreement with the theoretical value of 8 g per mole of electrons transferred for the formation of PtO or PtO₂. In 20 mM butanol and pentanol the slopes in the Pt oxide region are much smaller than in 0.5 M HClO₄, since, as said above, a large fraction of the charge, OP/(1+OP), is consumed in the electrooxidation of the alcohols, which does not contribute to the mass increase. These slopes in alcohol decrease with decreasing scan

Table 4
Mass change per mole of electrons transferred obtained as the slopes of Δm vs. ΔQ plots in Fig. 4

	Scan rate/V s ⁻¹	H _s	d.l.	ox
Base	0.1	10.8	22.5	7.43
	0.05	8.0	23.5	7.55
	0.02	7.2	17.0	6.69
Butanol	0.1	2.42	3.68	1.71
	0.05	2.02	3.35	1.21
	0.02	1.26	2.07	0.73
Pentanol	0.1		3.87	1.75
	0.05		3.15	1.27
	0.02		2.10	0.78

The alcohol concentration was 20 mM.

rate, indicating an increasing participation of alcohol electrooxidation, as was to be expected.

3.1.5. Effect of the hexanol concentration on the second CV with black Pt electrodeposits with hexanol admission at open circuit

Fig. 5 shows the second CVs and mass curves, obtained as in Section 3.1.4, for a black Pt/Au/Q electrode at 0.1 V s⁻¹ in 0.5 M HClO₄ (solid line) and in the presence of 5 (dashed line) and 20 mM (dotted line) hexanol. With increasing hexanol concentration, the hydrogen desorption charge decreases, the anodic oxidation charge increases, and in the negative scan the Pt oxide reduction charge decreases (Fig. 5A). Peak IV almost does not appear at this high scan rate. With forced coincidence of the mass at the positive potential limit, in the positive scan the mass in 20 mM hexanol is much lower than that in base electrolyte over the whole potential range (Fig. 5B). Furthermore, in the negative scan the mass decrease starts together with the scan with 20 mM hexanol, while with 5 mM hexanol it starts at lower potentials only, probably because with 20 mM hexanol there is a larger extent of chemical reduction of the Pt oxide by the alcohol. Similar results were observed for bright Pt/Q electrodes (not shown).

The initial mass at the starting potential is much lower with 20 mM hexanol than in base electrolyte, although with 5 mM hexanol it was even higher than in base. Probably the physisorption of hexanol (in the double layer region) increases significantly with concentration,

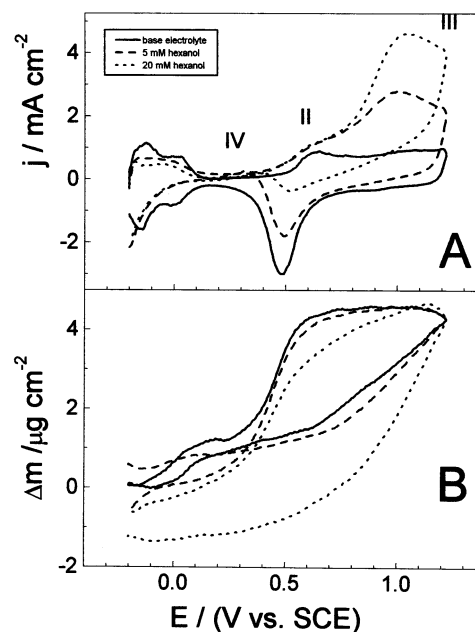


Fig. 5. Second cyclic voltammogram (A) and simultaneously recorded mass response (B) of a black Pt/Au/Q electrode at 0.1 V s⁻¹ in 0.5 M HClO₄. The alcohol was added to the electrolyte while the electrode was at open circuit and the scans were begun at the negative limit. $R_F = 12.1$.

leading to a stronger inhibition of the adsorption of water and/or ions. Furthermore, perhaps with 20 mM hexanol there is an increase of chemisorbed CO, which would preclude the adsorption of water and ions. This is supported by EMIRS results of Beden et al. [30], who found that poisoning by CO of methanol oxidation on smooth Pt electrodes is slight at low methanol concentrations, but very severe at higher concentrations.

3.2. Electrooxidation of hexanol at constant potential on a bright Pt/Q electrode

In order to confirm the chemical reduction of the Pt oxides by the alcohols, controlled potential experiments were carried out with bright Pt/Q electrodes in 0.5 M HClO₄. The results for controlled potentials of 0.3, 0.5, 0.7 and 0.9 V versus SCE are shown in Fig. 6A–D, respectively. The arrows show the moment at which hexanol was added to the electrolyte up to a final concentration of 8 mM, all the experiment being conducted under continuous nitrogen bubbling. Curves 1 show the response in the presence of hexanol, and curves 2, recorded in the absence of hexanol, have been included for comparison purposes. It can be seen that already at 0.4 V, the potential at which Pt oxidation starts, hexanol addition produces an increase of anodic current and a concomitant mass decrease. The simplest interpretation of this mass decrease is that hexanol reduces some Pt oxide chemically. Similar results were observed by Wilde and Zhang [16] for methanol oxidation at black Pt/Au/Q electrodes upon addition of methanol at different potentials, a chemical reaction between the oxide and methanol being proposed.

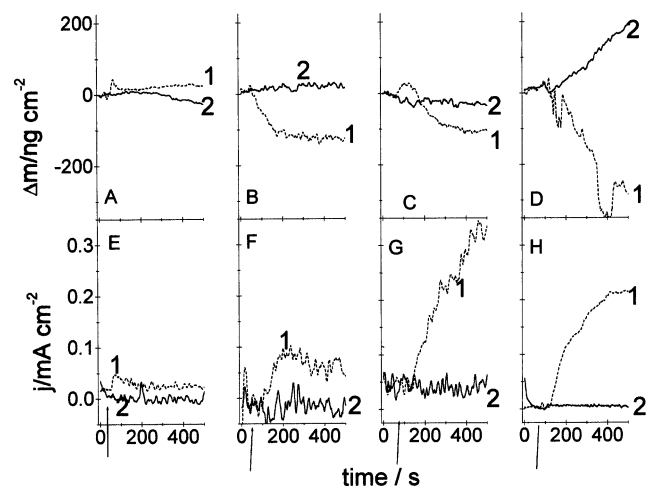


Fig. 6. Evolution with time of the mass change (Δm) (A–D) and of the simultaneously recorded current density (j) (E–H) in the presence (dashed lines (1)) and the absence (solid lines (2)) of 8 mM hexanol of a bright Pt/Q electrode held at the following potentials: (A) 0.3; (B) 0.5; (C) 0.7; and (D) 0.9 V vs. SCE. The moment of hexanol addition is indicated by an arrow. The electrolyte was 0.5 M HClO₄.

3.3. Influence of the admission potential on the electrooxidation of alcohols on smooth Pt

Due to the differences between the first and the second scans for the alcohol oxidation at a black Pt/Au/Q electrode, measurements with a smooth Pt disc were made admitting the alcohol at open circuit (Fig. 7) and at -0.22 V (Fig. 8). When the alcohol was admitted at open circuit in deaerated 0.5 M HClO₄ an immediate potential decrease down to 0.05 V versus SCE was observed, indicating that alcohol dissociative chemisorption, yielding chemisorbed H, had occurred. The CV obtained at 0.02 V s⁻¹ in the presence of 2 mM of alcohol (Fig. 7, solid line) shows, in comparison with that in 0.5 M HClO₄ (Fig. 7, dotted line), the well-known decrease in the hydrogen region due to chemisorbed residues produced by dissociative chemisorption of the alcohol [1], and consequently the absence of peak I, which is observed only with a CO-free Pt surface. Two oxidation peaks in the positive scan (peaks II and III) and one in the negative scan (peak IV) appear. Peak III is higher for heptanol and octanol, probably because of an increased physisorption prior to the electrooxidation, a decrease of the Pt oxide reduction peak also being observed for these two alcohols. $\theta_{\text{CO}}^{\text{H}}$ increases with chain length, while the OP is at a minimum for hexanol (Table 5).

If under the same experimental conditions the alcohols are admitted at -0.22 V, no decrease of the hydrogen desorption charge, together with the appearance of peaks I and IV, are observed for the five alcohols (Fig. 8), independently of the chain length. The current densities of peaks II and III depend hardly at all on chain length, and the decrease of the Pt oxide reduction peak with increasing chain length is far less than with open circuit admission. The CO coverages produced in peak I are lower than those produced by dissociative chemisorption of the alcohols at open circuit, while the OP values are higher (Table 6). Neither the CO coverage nor the OP value shows a definite influence of chain length.

4. Discussion

The electrooxidation of primary alcohols is a complex reaction, in which different intermediates and products may be involved in different potential regions, and, furthermore, more than one reaction can occur simultaneously. Although certainly neither CV nor EQCM techniques can provide information on the chemical nature of intermediates and products, a detailed analysis of the results can yield interesting insights on the processes involved. In this work the changes in the resonance frequency of the quartz crystal microbalance have been ascribed solely to mass changes, without

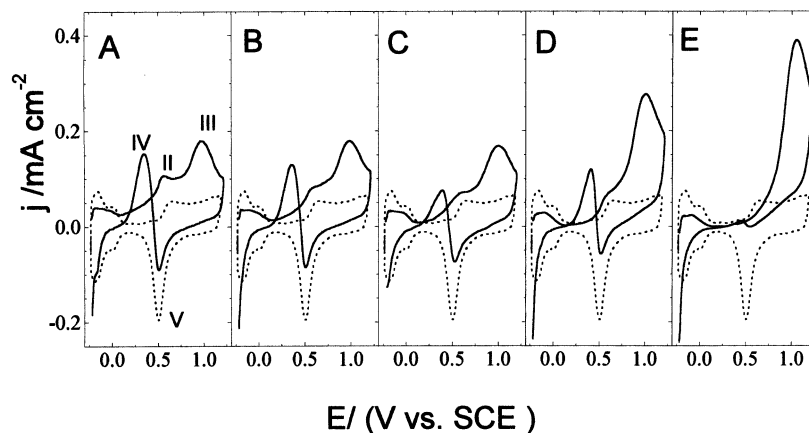


Fig. 7. Cyclic voltammograms of a smooth Pt electrode at 0.02 V s^{-1} in 0.5 M HClO_4 without (dashed lines) and with (solid line) 2 mM of: (A) *n*-butanol; (B) *n*-pentanol; (C) *n*-hexanol; (D) *n*-heptanol; and (E) *n*-octanol. The alcohols were admitted at open circuit and the scans were begun at the negative limit. $R_F = 2.3$.

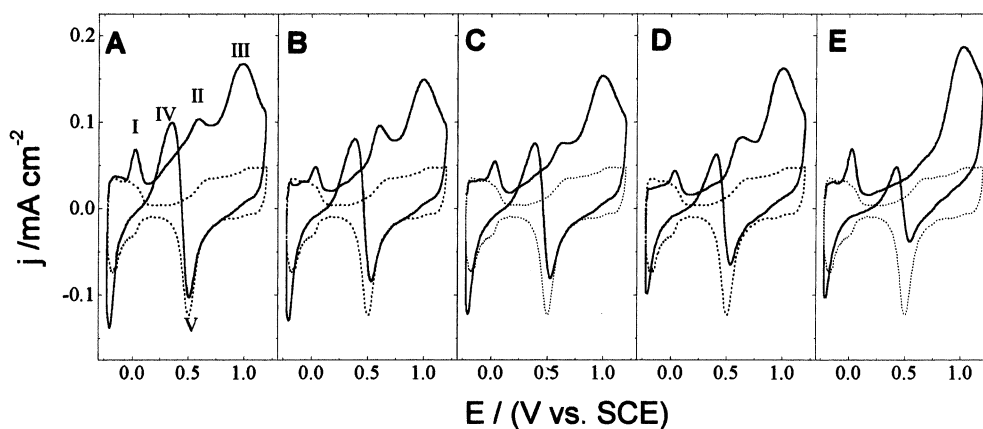


Fig. 8. First cyclic voltammograms of a smooth Pt electrode at 0.02 V s^{-1} in 0.5 M HClO_4 without (dashed lines) and with (solid line) 2 mM of: (A) *n*-butanol; (B) *n*-pentanol; (C) *n*-hexanol; (D) *n*-heptanol; and (E) *n*-octanol. The alcohols were added to the electrolyte while the electrode was held at -0.2 V (SCE) and the scans were begun at this potential. $R_F = 2.3$

considering the changes in the viscoelastic properties of the interface which could occur, especially with the longer-chain alcohols at concentrations near their solubility limit.

4.1. Chemical reduction by alcohols of anodic oxides of Pt

The potentiostatic experiments with bright commercial Pt/Q electrodes (Fig. 6) show unequivocally that at the same potential, 0.4 V , at which Pt oxidation starts, the addition of hexanol brings about an increase of anodic current, due to the electrooxidation of hexanol, and a simultaneous mass decrease. As said above, this mass decrease can be simply interpreted as being due to a chemical reduction by hexanol of some Pt oxide. It is difficult to envisage any other mechanism by which the mass of the electrode would be decreased by hexanol addition, since at 0.4 V or higher potentials the

adsorption of water and ions should be negligible as compared with the mass increase due to Pt oxide formation. As said in Section 1, according to the XPS studies of Li et al. [10] the Pt surface oxides formed at potentials below 1.0 V versus SCE are active catalysts for alcohol electrooxidation, providing the required oxygen atoms. These active Pt oxides would be present over most of the potential excursion in the CVs

Table 5
Parameters corresponding to the second positive scan at 0.02 V s^{-1} for a smooth Pt electrode in $0.5 \text{ M HClO}_4 + 2 \text{ mM}$ alcohol

Alcohol	$\theta_{\text{CO}}^{\text{H}}$	OP
Butanol	0.26	4.2
Pentanol	0.37	3.5
Hexanol	0.49	3.0
Heptanol	0.60	5.1
Octanol	0.71	5.9

Data from Fig. 7. $R_F = 2.3$.

Table 6

Parameters corresponding to the first positive scan at 0.02 V s^{-1} for a smooth Pt electrode in $0.5 \text{ M HClO}_4 + 2 \text{ mM}$ alcohol with alcohol admission at -0.22 V

Alcohol	$\theta_{\text{CO}}^{\text{I}}$	OP
Butanol	0.32	7.5
Pentanol	0.10	5.9
Hexanol	0.20	5.7
Heptanol	0.06	5.7
Octanol	0.20	5.9

Data from Fig. 8. $R_{\text{F}} = 2.3$.

presented here, since the positive potential limit was 1.2 V .

The increase of peak III and the decrease in peak IV with the alcohol concentration is further experimental evidence of chemical reduction of the Pt oxide. The rate of this reaction probably depends on the surface structure, as in the case of peak I.

4.2. Lack of activity of black electrodeposited Pt for the dissociative chemisorption of alcohols

The behaviour towards alcohol chemisorption of black electrodeposited Pt is completely different from that of smooth, massive Pt (Fig. 7) [1], since even with alcohol admission at open circuit, electrodeposited Pt showed no activity for the dissociative chemisorption of the alcohol, and consequently the first CV showed peak I, characteristic of a residue-free Pt surface (Fig. 1). This lack of activity of electrodeposited Pt for alcohol dissociation is also reflected in the open circuit potential, which did not decrease significantly upon alcohol addition, while, as is well known, the open circuit potential of smooth Pt is readily and substantially decreased by the dissociative adsorption of alcohols. Peak I does not appear in the second and subsequent CVs, in the same way as it occurs with smooth Pt.

A dramatic difference between electrodeposited and smooth Pt has been reported by Hilmi et al. [31], who found that while electrooxidation of different 2,3-butanediol stereoisomers on Pt produced different current densities on smooth Pt, all the isomers yielded about the same current density on a Pt/Pt electrode.

It has been postulated recently by Pron'kin et al. [13] that electrodeposited Pt has two types of sites, one type being similar to the sites on smooth Pt, and another type constituted by 'defective', low-coordination surface sites, with a high oxygen binding energy. Upon electrooxidation these two types of sites would form two types of Pt oxide, with low and high Pt–O binding energies, and therefore active and inactive, respectively, for the chemical oxidation of organic compounds.

The same model has been postulated by Mukerjee and McBreen [32] for conventional electrocatalysts of car-

bon-supported Pt with a particle size of $2.5\text{--}8.0 \text{ nm}$, within which range there are significant differences in the coordination degree of Pt atoms at the surface. Particles smaller than 5 nm have many Pt sites with low coordination, and therefore able to form a strong Pt–OH bond stable at potentials more negative than 0.8 V (RHE), inhibiting alcohol electrooxidation, which would explain the absence of peak I in the second scans (Fig. 2).

4.3. Dissociative chemisorption of alcohols on black electrodeposited Pt and on smooth Pt

Besides the absence of peak I in the second scan with black electrodeposited Pt, with the longer-chain alcohols there occurs a high decrease in initial mass in the hydrogen region as compared to that in base electrolyte (Fig. 2), this mass decrease increasing with the alcohol concentration. Since this mass decrease occurs with the longer chain alcohols only, it should be due to physisorption of these more hydrophobic alcohols in the double layer region during the negative scan of the first CV.

For smooth Pt $\theta_{\text{CO}}^{\text{H}}$, which measures the coverage of chemisorbed residues produced during the negative scan of the first cycle, increases monotonically with the chain length up to octanol (Table 5), whereas for Pt black it increases only up to hexanol (Table 2). It is remarkable that, with the exception of heptanol, the values are very similar for both Pt/Au/Q and smooth Pt electrodes, and, as a matter of fact, the values are identical for pentanol and hexanol.

Dissociative chemisorption of the alcohols is a process which occurs at fairly high potentials, at which the Pt surface contains oxide or hydroxide sites, and, in principle, the reactivity of the hydroxyl group of the alcohol should be independent of the chain length. However, the monotonic increase of $\theta_{\text{CO}}^{\text{H}}$ with chain length indicates that in the previous negative sweep there occurs, simultaneously with the dissociative chemisorption, a physisorption of the alcohols that obviously would increase with increasing chain length, i.e. with increasing hydrophobicity, of the alcohol. This physisorption would be the origin of the great mass decrease at the beginning of the second positive scan with pentanol–octanol, and of the increase of this effect with the alcohol concentration for the lower alcohols. The fact that the mass decrease is absent in the first positive sweep (Fig. 1) indicates that this physisorption takes place only on the freshly reduced Pt sites, since the rapidly increasing current in the double layer region after holding the potential at -0.22 V , both in the absence and presence of alcohol added at that potential (Fig. 1), indicates that the Pt surface after a potential hold is not exceedingly clean.

It should be stressed that the mass curve of black Pt/Au/Q electrodes in 0.5 M HClO_4 changes with repetitive

potential cycling [18,19] as a consequence of changes in the deposit structure, while the bright Pt/Q electrodes show a more stable behaviour. For this reason in this work the black Pt/Au/Q electrodes were subjected to a few potential cycles only.

5. Conclusions

The results presented here indicate the following:

- a) None of the alcohols tested became adsorbed on black Pt/Au/Q electrodes when they were admitted at a controlled potential of -0.22 V, since the electrode mass was unaffected by the alcohol addition. Probably this was due to contamination of the electrode surface during the potential hold, since all the reactants were p.a. grade and were used as received.
- b) With black Pt/Au/Q electrodes the initial mass at the beginning of the second scan was lower for pentanol–heptanol as compared with the initial mass in the first scan, which indicates that these longer, more hydrophobic alcohols physisorb on black electrodeposited Pt in the double layer region during the negative scan of the first CV, i.e. on freshly reduced, and thereby cleaned, Pt sites.
- c) Chemical reduction of the Pt oxides by the alcohols has been demonstrated unequivocally by controlled potential experiments with Pt/Q electrodes in 0.5 M HClO_4 . Hexanol addition at 0.4 V, the potential at which Pt oxidation starts, or higher potentials produces a concomitant mass decrease, the simplest interpretation of this decrease being that hexanol reduces the Pt oxide chemically.
- d) While primary alcohols chemisorb dissociatively on polished Pt at open circuit, producing chemisorbed residues that inactivate the electrooxidative dehydrogenation of alcohols that gives origin to peak I, they do not on black Pt electrodeposits, probably because many of the Pt atoms in the deposit have a low coordination, and therefore bind oxygen so strongly that the Pt oxide cannot react chemically with the alcohols.
- e) The mass curves show, as was to be expected from the CVs, that reduction of Pt oxide, but not its formation, becomes increasingly irreversible with increasing scan rate.

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